

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> : C07C 41/09, 41/50, 1/20		A1	(11) International Publication Number: WO 00/51957
			(43) International Publication Date: 8 September 2000 (08.09.00)
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(54) Title: ACID-CATALYSED REACTIONS			
(57) Abstract			
<p>The present invention relates to acid-catalysed reactions of alcohols to produce ethers, acetals, ketals or alkenes. The reactions are carried out in the presence of a heterogenous catalyst under near-GB0000672 or supercritical conditions of temperature and pressure. The reactions of the present invention have the benefit that improved yields and/or selectivities may be obtained. In some cases, products which are not readily available by conventional acid-catalysed reactions of alcohols may be obtained.</p>			

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## Acid-Catalysed Reactions

The present invention relates to acid-catalysed reactions for producing alkenes, ethers, acetals or ketals. Specifically the present invention relates to reactions for the formation of alkenes, ethers (including cyclic ethers), acetals and ketals in the presence of heterogeneous acid catalysts under near-critical or supercritical conditions.

In particular, the present invention seeks to provide improved acid-catalysed reactions of alcohols (whether aliphatic, aromatic or heterocyclic) to produce ethers, alkenes, acetals or ketals as required.

The use of acid catalysis in industry is widespread and of importance.

We have shown that reactions of industrial importance such as ether, acetal, ketal and alkene formation can be carried out under supercritical or near critical conditions of temperature and pressure using a heterogeneous acid catalyst with significant advantages. Their use in supercritical fluids has not previously been described.

Using supercritical fluids as a solvent eliminates the need for conventional organic solvents and hence gives environmental benefits. However, a more important consequence is that the reactions can be modified by using supercritical fluids to give surprisingly high yields and/or selectivities.

We have also found that certain products which are not easily accessible by conventional routes can be obtained more easily using the process of the present invention. Thus, whilst rearrangements may occur in conventional reactions we have found that certain reactions can be carried out under the conditions of

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the present invention without any significant rearrangement occurring. For example, ether formation in supercritical fluids under the conditions of the present invention can give rise to enhanced yields of  
5 n-alkyl ethers rather than the branched products which are obtained in conventional procedures.

### Ethers

Conventionally, the formation of ethers can be  
10 carried out via a wide number of classical routes e.g. Williamson Synthesis, dehydration of alcohols, alkylation of alcohols with inorganic esters, and alkylation with diazo compounds.

In the Williamson synthesis an alkyl halide is  
15 reacted with an alkoxide or aryloxy. This reaction therefore involves preforming the alkoxide from an alcohol by reaction with a strong base and subsequent reaction with an alkyl halide. This results in the generation of an equimolar amount of a halide salt  
20 which then must be disposed of. There are also the hazards associated with the handling of the alkyl halide in the case of volatile and/or toxic halides such as methyl iodide which is both a known carcinogen and very volatile.

25 In the case of reactions of alcohols with inorganic esters (e.g. the reaction of an alcohol with dimethyl sulfate), the inorganic esters are usually highly toxic. Again the alcohol has to be converted to the alkoxide using a strong base prior to the reaction.  
30 A further problem is the disposal of the aqueous effluent which can contain large amounts of inorganic salts.

The reaction of diazo compounds with alcohols is a cleaner reaction but suffers from the dangers

associated with the thermal decomposition of diazo compounds. Also, diazo compounds are expensive and so it is not practicable to carry out this reaction on an industrial scale except for very high value products.

5        One of the most cost-effective and atom-efficient processes for producing ethers is the dehydration of alcohols using an acid catalyst. This reaction is usually carried out in the liquid phase but suffers the drawback that, in the reaction of *n*-alcohols, the  
10       alcohol can rearrange from the primary to secondary and then to the tertiary carbocation, thereby giving a mixture of products. A further problem is that the use of homogeneous catalysts such as sulphuric acid require a separation or neutralisation step at the end of the  
15       process. The use of homogeneous catalysts means that these processes are usually carried out in batch or semi-batch reactors. The use of batch systems also gives increased down time for charging and discharging. There is also the disadvantage that the product will be  
20       a mixture of thermodynamic and kinetic products due to relatively long residence times in the reactor. Distillation or some other physical means of separation is therefore usually required to separate the products.

25       A number of other reactions are also carried out to form ethers, usually on a smaller scale, such as the reaction of a Grignard reagent with an acetal or cyclisation of alcohols with lead, silver or mercury salts all of which suffer from high cost and problems of waste disposal.

### 30       Acetals and Ketals

      The most widely used method of formation of acetals and ketals is the reaction of alcohols with aldehydes or ketones under acidic conditions which

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involves the removal of water. These reactions are usually carried out in an excess of the alcohol or in an inert solvent. The conventional process therefore presents the problem of removing excess reagent and the catalyst must also be separated from the mixture if a homogenous catalyst is used.

### Alkenes

The industrial preparation of alkenes is normally carried out by dehydrogenation over noble metal catalysts or cracking reactions or dehydration reactions using inorganic acids. Such reactions present the problems of removal of catalyst, reaction solvent and distillation to purify products.

We have found that the use of supercritical fluids for the replacement of conventional solvents not only has significant environmental benefits but also leads to cleaner, higher yielding reactions.

Although the mechanism of the reactions is not fully understood it is believed that mass transport effects play a role in the observed improvements in yield and/or product selectivity. Surprisingly, the use of a heterogeneous catalyst in place of a homogeneous catalyst under near-critical or supercritical reaction conditions does not render the reaction ineffective. Instead we have found that the reactions benefit from improved yields and/or selectivity in product formation. This is so despite the expectation that the relatively severe conditions at or near the supercritical point of the reaction medium may give rise to a mixture of products because the reactants have sufficient energy to react via several different pathways.

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One consequence of using the heterogeneous catalyst is that there is no need for complicated separation procedures to liberate the product from the reaction mixture and catalyst. This represents quite a benefit in terms of both the time savings and cost savings of the present invention.

We have thus found that it is possible by using a combination of supercritical fluids and a heterogeneous catalyst (e.g. the Deloxan ASP catalyst from Degussa or Acidic Amberlyst resin from Rohm and Haas) in a continuous flow reactor to carry out a number of reactions rapidly and cleanly. These reactions can often be performed in high yield and take place under near-critical or supercritical conditions.

According to the present invention, there is provided a process in which an organic compound having the formula  $R^1CH_2OH$ ,  $R^1R^2CHOH$ , or  $R^1R^2R^3COH$  is exposed, optionally in the presence of one or more further organic compounds having the formula  $R^4CH_2OH$ ,  $R^5R^6CHOH$ ,  $R^7R^8R^9COH$  or  $R^{10}R^{11}CO$ , to a heterogenous catalyst which is able to provide a source of acid in a continuous flow reactor under supercritical or near-critical conditions with the result that an ether, acetal, ketal or alkene product is formed, wherein the conditions of temperature, pressure, and flow rate are independently controlled, and wherein each of  $R^1$  to  $R^{11}$  is independently selected from: hydrogen, hydroxyl, or an optionally substituted alkyl, alkenyl, alkynyl, aralkyl, cycloalkyl, cycloalkenyl, aryl or heterocyclic group.

Aliphatic and aromatic alcohols are preferred because they give cleaner reactions, with aliphatic alcohols being most preferred on the grounds of ease of use and lower occurrence of side products.

It is preferred that each of  $R^1$  to  $R^{11}$  when present is an alkyl group which may be optionally substituted. Since the process of the present invention is applicable to diols, triols and higher alcohols as well as alcohols, it is particularly preferred that the optional substituent, when present, on one of the groups  $R^1$  to  $R^{11}$  is hydroxyl. It is also preferable, in order to avoid the risk of unwanted side products, that the total number of alcohol groups within the organic compound does not exceed three.

When any of the  $R^1$  to  $R^{11}$  groups are optionally substituted, the substituent groups which are optionally present may be any conventional substituent provided that any such substituent is not incompatible with alcohol functionality or with the reaction conditions.

Generally, when any of the  $R^1$  to  $R^{11}$  groups represents an optionally substituted alkyl group each group may independently be linear or branched and suitably contain 1 to 10, preferably 1 to 6 carbon atoms in the carbon chain, not including any optional substituent which may be present.

In relation to alkyl groups, specific examples of such optional substituents include halogen atoms and nitro, hydroxyl,  $C_{1-4}$  alkyl,  $C_{1-4}$  haloalkyl (especially  $CF_3$ ),  $C_{1-4}$  alkoxy,  $C_{1-4}$  haloalkoxy and ( $C_{1-4}$  alkoxy) carbonyl groups. Of these, hydroxyl and  $C_{1-4}$  haloalkyl are preferred. It is preferred, however, that when any of groups  $R^1$  to  $R^{11}$  is alkyl that the alkyl moiety is unsubstituted.

In relation to a phenyl moiety, optional substituents include halogen atoms, and nitro, hydroxyl,  $C_{1-4}$  alkyl,  $C_{1-4}$  haloalkyl (especially  $CF_3$ ) and  $C_{1-4}$  alkoxy groups.



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In general, 1 to 3 optional substituents may suitably be employed. Halogen atoms when present are preferably fluorine.

5 Where the starting materials for the reaction may exist in isomeric form the reaction of the present invention is applicable to all such optical or geometric isomers.

Suitable catalysts include Deloxan acid catalysts (Ex. Degussa-Hüls AG), zeolites, metal oxides,  
10 molecular sieves, clays, sulfonic acid derivatives, or other equivalent heterogeneous sources of a Brønsted acid (e.g. Amberlyst resin). The catalyst is ideally supported on an inert carrier. Preferably the catalyst contains sulfonic acid groups, and more preferably the  
15 catalyst is a Deloxan catalyst or an equivalent thereof.

The reactions of the present invention are preferably carried out in a single homogeneous phase. However, in reactions where water is generated this may  
20 separate out as a separate phase. This separation can be helpful to the reaction. Preferably, the reactions are performed in the supercritical phase.

In the context of the present invention, the lower limit suitable for supporting the reaction is a  
25 condition of temperature and pressure below or near to (perhaps at) the critical point of the solvent. When a fluid reaches its critical point its density is substantially decreased relative to its density at its boiling point at normal pressure. Small changes in  
30 pressure or temperature near the critical point cause additional changes in density. The process of the present invention will operate in the fluid at temperatures and pressures below the critical point but at which the density is sufficient to ensure solvation

of reagents.

The upper limit of temperature and pressure is governed only by limitations of the apparatus.

5 In practice, the choice of the near critical or supercritical fluid will depend upon the solubility of the organic compound in the fluid since a function of the supercritical or near-critical fluid is to act as a solvent for the reagents. In some cases, however, it may be particularly convenient for the near-critical or  
10 supercritical medium to be simply the alcohol itself (and the other optional reactants when present). However, the use of a separate near-critical or supercritical fluid is generally preferred.

15 Particularly favoured media include carbon dioxide, alkanes such as ethane, propane and butane, alkenes, and saturated halocarbons such as hydrofluorocarbons and trichlorofluoromethane.

The near-critical or supercritical reaction medium when present, may be a mixture of two or more fluids  
20 having critical points which do not require commercially unacceptable conditions of temperature and pressure in order to achieve the necessary conditions for reaction according to the present invention. For example, a mixture of carbon dioxide with an alkane  
25 such as propane may be employed close to or above the theoretical critical point of the mixture.

The alcohol starting material, if not a free-flowing liquid in its normal state may be dissolved in a solvent for the purpose of introducing the alcohol  
30 into the reactor. This solvent may be present in addition to or in place of the solvent which is to be the supercritical or near-critical reaction medium. Alternatively as stated above, the alcohol itself, and any further optional components of the reaction

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mixture, may be the near-critical or supercritical reaction medium.

Product formation may be monitored *in-situ* by means of IR spectroscopy using a suitably positioned IR cell, or by gas or liquid chromatography performed on samples drawn from the reactor periodically.

We are thus able to form ethers from primary and secondary alcohols with high conversion and good selectivity for *n*, or branched, products. Surprisingly *n,n* ethers can be formed by dehydration of *n*-alcohols with little or no rearrangement. In the case of phenolic compounds it is possible by altering the reaction conditions to favour ether formation over Friedel-Crafts alkylation and vice-versa.

We have also demonstrated that it is possible to form acetals and ketals under similar supercritical or near-critical conditions as those employed for ether formation. In the case of branched alcohols, it is also possible to select conditions in which the corresponding alkene is obtained in high yield in preference to the ether product.

There is also little requirement for excess alcohols to be used in the process of the present invention because of the excellent conversion rates; this simplifies purification of the products.

The reactions are performed using a continuous flow reactor (preferably tubular reactor). It is therefore possible to control the residence time, and also the other reaction parameters independently. This allows greater control of the reaction resulting in more efficient and also more selective reactions than can be achieved in the conventional processes.

The present invention will now be described by way

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of example only with reference to Figure 1. Figure 1 is a schematic diagram of a continuous flow reactor according to the present invention.

5 The substrate 1, which is dissolved in an appropriate inert solvent (for example an alkane such as hexane) if it is not a free-flowing liquid or if it is a solid, is pumped into mixer 2 which is a mixing vessel. The mixer 2 may include a stirrer (not shown). However, mixing of substrate 1 and fluid 3 may equally  
10 be effected without the use of stirrer. The substrate 1 is mixed with fluid 3 which is delivered from a reservoir via a pump to mixer 2. Where required, an additional reagent can be added via the same or another pump to mixer 2 with the ratio of the reagents being  
15 independently varied as required.

The temperature and the pressure in the mixer is adjusted to a temperature and pressure close to or above the critical point of the fluid 3 as required.

Heating means are provided in the mixer for this  
20 purpose. The mixture is then passed into reactor 5 which contains a heterogeneous catalyst (not shown) fixed on a suitable support. A means of controlling the pressure in the reactor is also included. The catalyst provides a source of Brønsted acid to the  
25 reaction mixture as the pressurised mixture passes over the catalyst.

After an appropriate mean residence time in reactor 5, the fluid 3, which now contains the product, is passed into pressure reduction unit 6. The products  
30 7 are removed via a take-off tap after passing through pressure reduction unit 6. The flow rate of reactants through reactor 5 is controlled by a valve (not shown) in pressure reducer 6. Fluid 3 is vented through a relief pipe 8 for subsequent recycling or

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disposal.

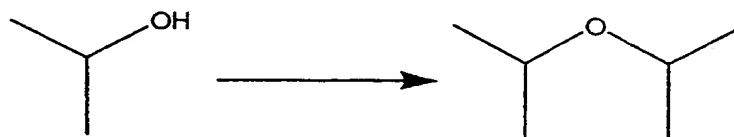
The parameters of a typical reaction might involve a system pressure of 40-300 bar (this will of course depend on the reaction medium) and the flow rate of the reagents is typically in the range of 0.5 to 20.0 ml/min. The reactor temperature is usually in the range of 30-350°C (again this will depend on the reaction medium) and the flow rate of supercritical or near critical fluid is usually in the range of 0.65 to 1.65 l/min of gaseous flow at atmospheric pressure-for a 10ml reactor.

The present invention will now be illustrated by the following examples in which the temperature is the catalyst bed temperature and the solvent flow is given as gaseous flow at atmosphere pressure.

#### Example 1

##### iso-Ether Formation

Isopropyl alcohol was exposed to a Deloxan ASP 1/7 acid catalyst (available from Degussa-Hüls AG) under the conditions given below in a continuous flow reactor. The volume of the reactor was 10 ml and the flow rate of the solvent was 0.65 L/min.

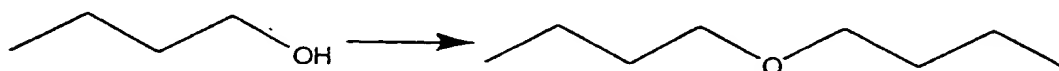


Temp (°C)	Pressure (Bar)	Substrate Flow Rate (ml/min)	Solvent	Yield (%)
200	200	0.5	CO <sub>2</sub>	29

## Example 2

*n*-Ether Formation

*n*-Butanol was exposed to an Amberlyst 15 acid catalyst under the conditions given below in a continuous flow reactor. The volume of the reactor was 20 ml and the flow rate of the solvent was 0.65 L/min.

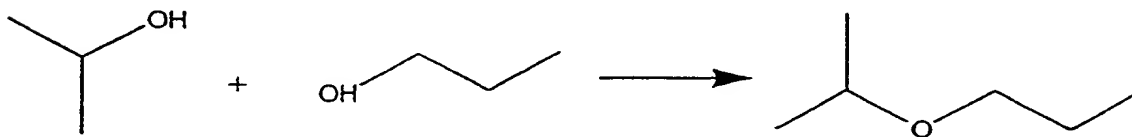


Temp (°C)	Pressure (Bar)	Substrate Flow Rate (ml/min)	Solvent	Yield (%)
200°C	200	0.5	CO <sub>2</sub>	60

## Example 3

## Mixed Ether Formation

Isopropanol and *n*-propanol in the ratio of 1.2 parts isopropanol to 1.0 parts *n*-propanol were exposed to a Deloxan ASP 1/7 acid catalyst (Degussa-Hüls AG) under the conditions given below in a continuous flow reactor. The reactor volume was 20 ml and the flow rate of the solvent was 0.65 L/min.



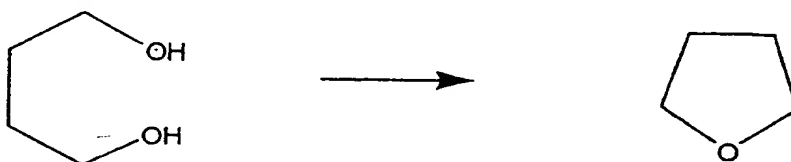
Temp (°C)	Pressure (Bar)	Substrate Flow Rate (ml/min)	Solvent	Yield (%)
150	200	0.5	CO <sub>2</sub>	41

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## Example 4

## Cyclic Ether

1,4-butanediol was exposed to a Deloxan ASP 1/7 acid catalyst (available from Degussa-Hüls AG) under the conditions given below in a continuous flow reactor. The reactor volume was 10ml and the solvent flow rate was 0.65 L/min.

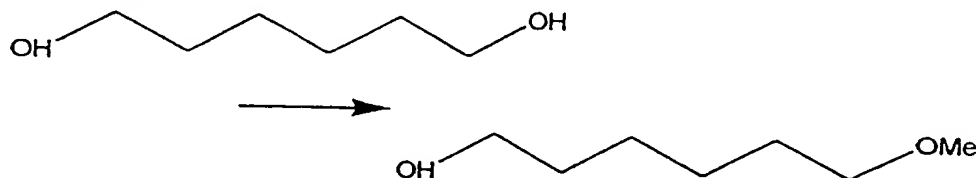


Temp (°C)	Pressure (atm)	Substrate Flow Rate (ml/min)	Solvent	Yield (%)
200	200	0.5	CO <sub>2</sub>	100
150	100	0.5	CO <sub>2</sub>	100
125	100	0.5	CO <sub>2</sub>	87
200	100	2.0	CO <sub>2</sub>	93

## Example 5

## Mono-Etherification of Diols

1,6-Hexanediol and methanol in the ratio of 1.0 part 1,6 hexanediol to 1.1 part methanol were exposed to a Deloxan ASP 1/7 acid catalyst (Degussa-Hüls AG) under the conditions given below in a continuous flow reactor. The reactor volume was 10 ml and the flow rate of the solvent was 0.65 L/min.

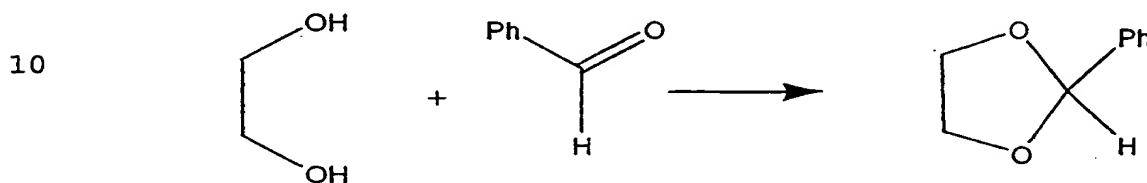


Temp (°C)	Pressure (atm)	Substrate Flow Rate (ml/min)	Solvent	Yield (%)	Di-ether (%)
100	200	0.5	CO <sub>2</sub>	32	13
200	200	0.5	CO <sub>2</sub>	65	6

## Example 6

## Acetal Formation

1,2-Ethanediol and benzaldehyde in the ratio of 2.0 parts benzaldehyde to 1.0 part 1,2-ethanediol were exposed to a Deloxan ASP 1/7 acid catalyst (Degussa-Hüls AG) under the conditions given below in a continuous flow reactor. The reactor volume was 10 ml and the flow rate of solvent was 0.65 L/min.



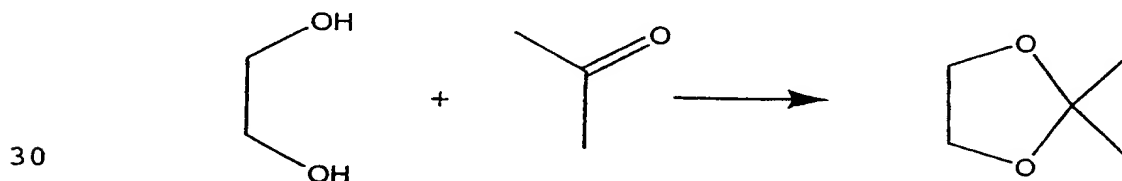
15

Temp (°C)	Pressure (atm)	Substrate Flow Rate (ml/min)	Solvent	Yield (%)
100	200	0.5	CO <sub>2</sub>	89
200	200	0.5	CO <sub>2</sub>	80

## Example 7

## Ketal Formation

1,2-Ethanediol and acetone in the ratio of 2.0 parts acetone to 1.0 part 1,2 ethanediol were exposed to a Deloxan c ASP 1/7 acid catalyst (Degussa-Hüls AG) under the conditions given below in a continuous flow reactor. The reactor volume was 10 ml and the flow rate of solvent was 0.65 L/min.



Temp (°C)	Pressure (atm)	Substrate Flow Rate (ml/min)	Solvent	Yield (%)
150	200	0.5	CO <sub>2</sub>	61

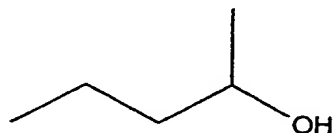


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## Example 8

## Alkene Formation

2-Pentanol was exposed to a Deloxan ASP 1/7 catalyst  
(Degussa-Hüls AG) under the conditions given below in a  
continuous flow reactor. The reactor volume was 10ml  
and the flow rate of solvent was 0.65 L/min.



2-Pentene

Temp (°C)	Pressure (atm)	Substrate Flow Rate (ml/min)	Solvent	Pentene (%)
200	200	0.5	CO <sub>2</sub>	100

## Claims

1. A process in which an organic compound having the formula  $R^1CH_2OH$ ,  $R^1R^2CHOH$  or  $R^1R^2R^3COH$  is exposed, optionally in the presence of one or more further organic compounds having the formulae  $R^4CH_2OH$ ,  $R^5R^6CHOH$ ,  $R^7R^8R^9COH$  or  $R^{10}R^{11}CO$ , to a heterogeneous catalyst which is able to provide a source of acid in a continuous flow reactor under supercritical or near-critical conditions with the result that an ether, acetal, ketal or alkene product is formed, wherein the conditions of temperature, pressure, and flow rate are independently controlled, and wherein each of  $R^1$  to  $R^{11}$  is independently selected from: hydrogen or hydroxyl; an optionally substituted alkyl, alkenyl, alkynyl, aralkyl, cycloalkyl, cycloalkenyl, or aryl; or a heterocyclic group.

2. A process according to claim 1, wherein each of  $R^1$  to  $R^{11}$  when present is an optionally substituted alkyl group, preferably each of the alkyl groups independently containing not more than 10 carbon atoms in the carbon chain (excluding optional substituents if present).

3. A process according to claim 1 or 2, wherein the total number of alcohol groups within the organic compound does not exceed three.

4. A process according to claim 1, 2 or 3, wherein the reaction is performed under supercritical conditions.

5. A process according to any preceding claim, wherein the organic compound of formula  $R^1CH_2OH$ ,  $R^1R^2CHOH$  or  $R^1R^2R^3COH$ , and optionally one or more of the compounds of formulae  $R^4CH_2OH$ ,  $R^5R^6CHOH$ ,  $R^7R^8R^9COH$  or  $R^{10}R^{11}CO$ , is dissolved in a fluid selected from: carbon dioxide, propane, an alkene, an alkyne, hydrocarbon, halocarbon, nitrogen, or a mixture of any of these.

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6. A process according to claim 1, 2, 3 or 4, wherein the organic compound is the supercritical or near-critical fluid.

5 7. A process according to any preceding claim, wherein the catalyst is selected from: zeolites, metal oxides, molecular sieves, clays, or sulfonic acid derivatives.

8. A process according to claim 7, wherein the catalyst is supported on an inert carrier.

10 9. A process according to claim 7 or 8, wherein the catalyst includes a promoter.

10. A process according to any of claims 7, 8 or 9, wherein the acidity of the catalyst is provided by a sulfonic acid group.

15 11. A process according to any preceding claim, wherein the reaction conditions are controlled in such a way that the products are selectively formed in high yield with insignificant rearrangement.

20 12. A process according to claim 11, wherein the reactant molecules are aliphatic and/or aromatic alcohols, preferably aliphatic alcohols.

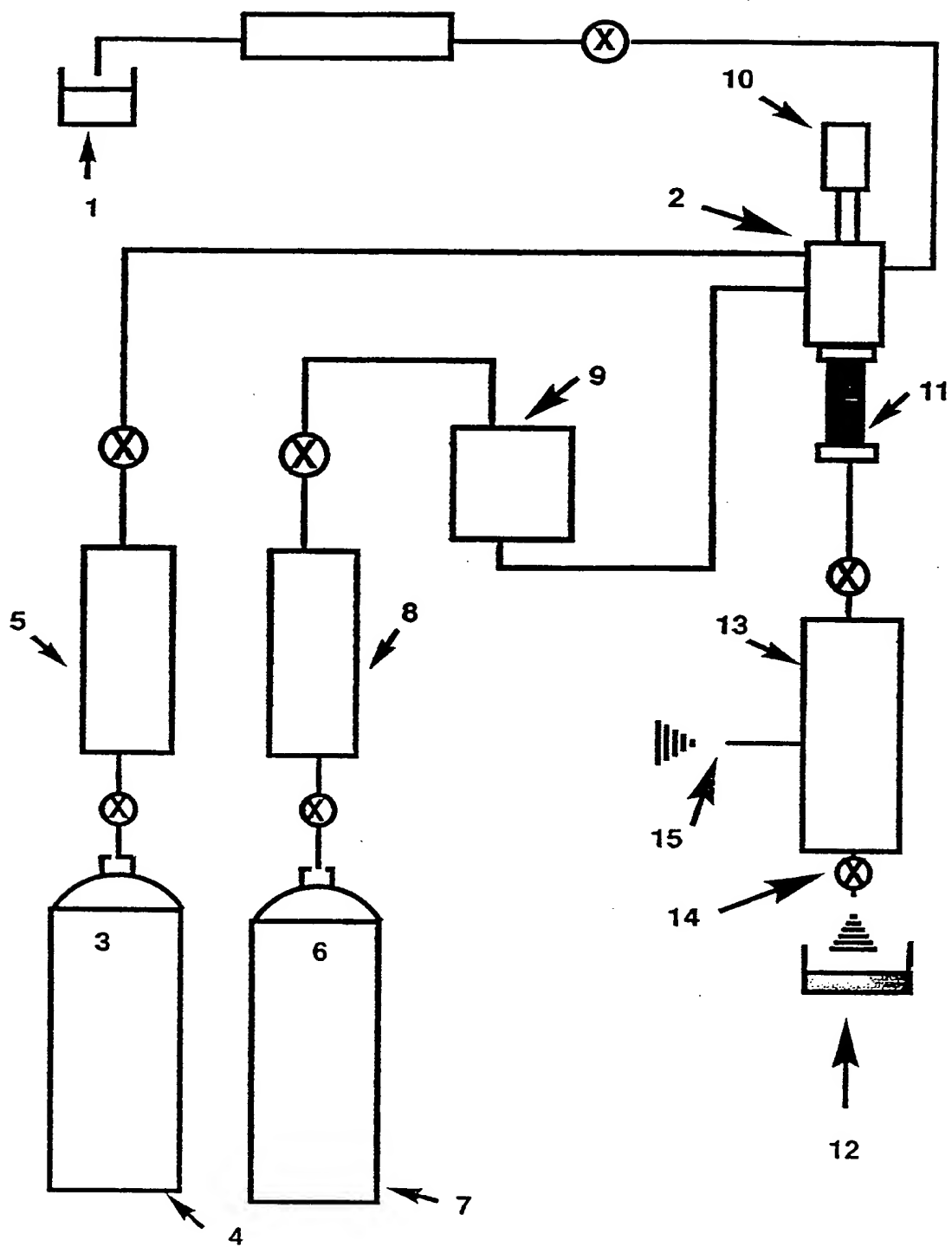
13. A process according to any preceding claim, in which the product is an ether.

25 14. A process according to claim 13, in which the reactant(s) and the product are straight-chain n-alkyl molecules.

30 15. A process according to claim 11 or 12, wherein the reaction conditions can be controlled in such a way that a particular alcohol is converted into an alkene in preference to an ether.

16. A process according to any preceding claim, in which the reactant(s) form a single homogeneous phase.

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/00673

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C41/09 C07C41/50 C07C1/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 5 831 116 A (WILLEY RONALD J ET AL) 3 November 1998 (1998-11-03) the whole document	1-16
A	EP 0 652 202 A (JAPAN RES DEV CORP ;IKARIYA TAKAO (JP)) 10 May 1995 (1995-05-10) page 3 -page 4	1-16
A	P. KRAMMER ET AL: "Untersuchungemn zum Synthesepotential in überkritischem Wasser" CHEMIE INGENIEUR TECHNIK, vol. 70, no. 12, 1998, pages 1559-1563, XP000791730 Weinheim page 1561 -page 1562	1-16

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

23 May 2000

Date of mailing of the international search report

07/06/2000

Name and mailing address of the ISA

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# INTERNATIONAL SEARCH REPORT

Interr. 1st Application No

PCT/GB 00/00673

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>GRAY, WILLIAM K. ET AL: "The Continuous Acid-Catalyzed Dehydration of Alcohols in Supercritical Fluids: A New Approach to the Cleaner Synthesis of Acetals, Ketals, and Ethers with High Selectivity"  J. AM. CHEM. SOC. (1999), 121(46),  10711-10718 , XP000887316  page 10711; tables 2-6</p>	1-16

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5831116 A	03-11-1998	NONE	
EP 0652202 A	10-05-1995	JP 2927677 B	28-07-1999
		JP 7330666 A	19-12-1995
		JP 2962649 B	12-10-1999
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		JP 2774076 B	09-07-1998
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		US 5639910 A	17-06-1997
		US 5763662 A	09-06-1998
		US 5869739 A	09-02-1999